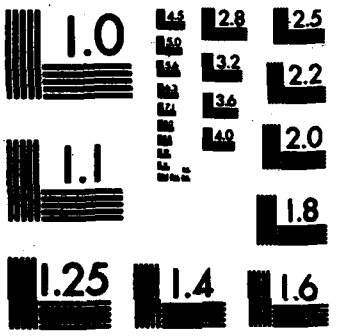
AD-A135 588 TDPAC (TIME DIFFERENTIAL PERTURBED ANGULAR CORRELATIONS) STUDY OF LIQUID A.. (U) OREGON STATE UNIV CORVALLIS DEPT OF PHYSICS D K GASKILL ET AL. 10 NOV 83 1/1

UNCLASSIFIED TR-5 N00014-79-C-0668 F/G 7/4 NL



OFFICE OF NAVAL RESEARCH/CHEMISTRY

Contract N00014-79-C-0668

Task No. NR 056-721

TECHNICAL REPORT NO. 5

TDPAC Study of Liquid and Amorphous $Se_{1-x}Te_x$ Alloys

by

D. K. Gaskill, John A. Gardner, K. S. Krane, and R. L. Rasera

Prepared for Publication

in the

Journal of Non Crystalline Solids

Proceedings of the 1983 International Conference

on Liquid and Amorphous Metals

Oregon State University
Department of Physics
Corvallis, Or.

November 10, 1983

TDPAC STUDY OF LIQUID AND AMORPHOUS $Se_{1-x}Te_x$ ALLOYS*

D.K. GASKILL, JOHN A. GARDNER, K.S. KRANE, AND R.L. RASERA**
Department of Physics, Oregon State University, Corvallis, OR 97331 USA

A time differential perturbed angular correlation study on several liquid and amorphous splat-quenched $Se_{1-x}Te_x$ alloys was performed using dilute ^{111}Cd as the tracer. The liquid spectra exhibits an attenuation factor, λ_{22}, consistent with the motional narrowing approximation. The attenuation factor is proportional to the motional correlation time t_c, multiplied by the average square electric quadrupole frequency, $\langle\nu_Q^2\rangle$. ν_Q has been characterized in amorphous splat-quenched Se and Te, allowing t_c to be computed for these two liquids from the measured λ_{22}. Spectra in both amorphous Se and Te arise from two distinguishable sites with quadrupole frequencies similar to the sites in compounds of Se or Te with In.

We describe here an application of time differential perturbed angular correlation (TDPAC) to the study of molecular dynamics in liquid Se, Te, and $Se_{1-x}Te_x$ alloys. When combined with TDPAC spectra on corresponding amorphous solids, these measurements yield a hyperfine correlation time t_c for the tracer nucleus. t_c is approximately equal to the smallest of the characteristic times of molecular rotation, chalcogenbond-breaking, or tracer diffusion. Some of the data presented here on liquid Se and Se-rich alloys have been described previously.[1,2]

The radioactive tracer used in this work was ^{111}In whose relevant nuclear characteristics are given in Table 1. This tracer decays by electron

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: Technical Report #5	2. GOVT ACCESSION NO.: AD-A135588
3. RECIPIENT'S CATALOG NUMBER:	
4. TITLE (and Subtitle): TDPAC Study of Liquid and Amorphous $Se_{1-x}Te_x$ Alloys	5. TYPE OF REPORT & PERIOD COVERED: Interim
	6. PERFORMING ORG. REPORT NUMBER:
7. AUTHOR(s): D. K. Gaskill, John A. Gardner, K. S. Krane, and R. L. Rasera	8. CONTRACT OR GRANT NUMBER(s): N00014-79-C-0668
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Oregon State University, Corvallis, OR 97331	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: NR-056-721
11. CONTROLLING OFFICE NAME AND ADDRESS: Office of Naval Research/Chemistry, Arlington, VA 22217	12. REPORT DATE: November 10, 1983
	13. NUMBER OF PAGES: 10
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office):	15. SECURITY CLASS. (of this report): Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE:

16. DISTRIBUTION STATEMENT (of this Report)

Approve for public release, distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

To be published in Journal of Non Crystalline Solids, proceedings of the 1983 International Conference on Liquid and Amorphous Metals

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Time differential perturbed angular correlations
liquid $Se_{1-x}Te_x$
amorphous $Se_{1-x}Te_x$

LAMBDA

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A time differential perturbed angular correlation study on several liquid and amorphous splat-quenched $Se_{1-x}Te_x$ alloys was performed using dilute ^{111}Cd as the tracer. The liquid spectra exhibits an attenuation factor, λ_{22}, consistent with the motional narrowing approximation. The attenuation factor is proportional to the motional correlation time t_c, multiplied by the average square electric quadrupole frequency, $\langle\omega_Q^2\rangle$. ω_Q has been characterized in amorphous splat-quenched Se and Te, allowing t_c to be computed for these two liquids from the measured λ_{22}. Spectra in both amorphous Se and Te arise from two distinguishable

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

LAMBDA

NU

NU SUB Q

sites with quadrupole frequencies similar to the sites in compounds of Se or Te with In.

Parent half-life	2.83 days
Energies of γ-γ cascade	171-245 keV
Nuclear spin sequence	$\frac{7+}{2} - \frac{5+}{2} - \frac{1+}{2}$
Angular correlation coefficients:	
A_{22}	-0.180(2)
A_{44}	+0.002(3)
Intermediate nuclear state:	
half-life	84 nsec
spectroscopic nuclear quadrupole moment	+0.83(13) b

TABLE I. Summary of relevant nuclear characteristics of radioactive probe nuclide $^{111}In \rightarrow {}^{111}Cd$. All data taken from S. Raman and H. J. Kim, Nucl. Data B6, 39 (1971), except quadrupole moment which is from P. Herzog et al., Z. Phys. A 294, 13 (1980).

capture to an excited state of ^{111}Cd, which then decays to its ground state by emitting two successive γ-rays. The emission directions of these γ-rays are strongly correlated. This correlation is perturbed if the nucleus is subject to an external electric field gradient during the time between the emission of the first and second γ-rays. The TDPAC measurement is intended to determine the time dependence of the perturbation of the angular correlation.

Liquid samples were made by placing approximately 50 mg. of the appropriate alloy into a 3 mm diameter quartz tube, adding a few drops of (commercially-obtained carrier-free) ^{111}In-containing HCl solution, evaporating the water, evacuating and sealing the capsule. Experimental measurements were made after the sample had been homogenized at approximately 900°C for 24 hours. These samples were not allowed to freeze

until the series of measurements was complete. The amorphous samples were made by splat-quenching at 78K and were maintained at that temperature until all runs were complete. The experimental setup for the TDPAC measurements consists of four NaI(Tl) scintillation counters, arranged in fixed positions symmetrically in the horizontal plane about the sample furnace or dewar. Delayed coincidences of the 171-245 keV cascade were detected for interdetector angles θ=90° and 180° by standard fast-slow coincidence circuits. The resulting four spectra were stored in separate memory banks of a multichannel analyzer computer as a function of the time delay t between the two γ-ray emissions. After data were collected for approximately 24 hours, the ratio,

$$R(t) = \frac{2}{3} \left[\frac{C_1(180°,t)\, C_4(180°,t)}{C_2(90°,t)\, C_3(90°,t)} \right]^{1/2} - 1 \qquad (1)$$

was computed. Here the $C_i(\theta,t)$, i=1 to 4, are the time spectra collected by different detector combinations corrected for random coincidences. Representative R(t) spectra are shown in Figures 1-3 for liquid Se, liquid Te, and two amorphous splats, respectively. R(t) is related to the nuclear anisotropy A_{22} and the "perturbing function" $G_{22}(t)$ by

$$R(t) = \frac{A_{22}G_{22}(t)}{1 - \frac{1}{2} A_{22}G_{22}(t)} \quad . \qquad (2)$$

In solids, the electric field gradient is independent of time, and $G_{22}(t)$ is given by[3]

$$G_{22}(t) = S_{20} + \sum_{i=1}^{3} S_{2i} \cos(\omega_i t) \exp\left(-\frac{1}{2} \delta^2 \omega_i^2 t^2\right), \qquad (3)$$

where ω_i, i=1 to 3 for Cd, are functions of the quadrupolar frequency ν_Q and electric field gradient (EFG) anisotropy. δ is a measure of the frequency spread due to variations of the EFG in materials which are not

perfect crystals. The S_{2i}, i=0 to 3, depend on the average orientation of the EFG principal axes. Frequently nuclei occupy sites with differing EFGs, and if so, the observed $G_{22}(t)$ will be the appropriately weighted sum over all sites.

In liquids, molecular reorientation is normally rapid on the (nsec) time scale of the measurements, and the static assumption described above is not correct. If fluctuations are sufficiently rapid, the interaction can be treated in the motional narrowing approximation which yields the simple result,[4]

$$G_{22}(t) = e^{-\lambda_{22} t} \quad , \tag{4}$$

where for Cd,

$$\lambda_{22} = \frac{63}{250} \pi^2 \, t_c \, \langle \nu_Q^2 \rangle \tag{5}$$

Here t_c is the hyperfine field correlation time, and $\langle \nu_Q^2 \rangle$ is the average square quadrupole frequency. The data shown in Figs. 1 and 2 follow the simple exponential decay predicted by the above formula. Significantly more structure is evident for the amorphous samples whose spectra are shown in Fig. 3.

Fig. 4 shows the λ_{22} values obtained by fitting the liquid data to Eq. 4. For liquid Te, λ_{22} could be measured accurately only in the supercooled temperature range where it follows an activated temperature dependence with activation energy 0.56 eV. At lower temperatures, λ_{22} for the Se-rich liquids also follows an activated temperature dependence with a concentration-independent activation energy of 0.36 eV.

In order to compute t_c *from* λ_{22}, $\langle \nu_Q^2 \rangle$ *must be known. To the* extent that the average surroundings of the In/Cd tracer atom are the same in the liquid and amorphous solid, ν_Q can be found from the TDPAC

spectrum of the splat-quenched solid by fitting to Eq. 3. TDPAC spectra have been measured only on pure amorphous Se and Te. In each case, single-site fits were not adequate, but a two-site fit provided reasonably good agreement with experiment. For amorphous Se, approximately 70% of the tracer atoms are found to have quadrupolar frequency ν_Q = 110 MHz and 30% have ν_Q=70 MHz. For amorphous Te, approximately 70% have ν_Q = 130 MHz and 30% have ν_Q = 70 MHz. δ is of order 15% for all sites. This result indicates that in the two amorphous solids, In can occupy sites with two different near-neighbor configurations. The quadrupolar frequencies of the two sites in amorphous Se and Te are approximately the same as the frequencies of the two sites in In_2Se_3 and In_2Te_5 respectively.[5,6]

With these results, $\langle\nu_Q^2\rangle^{1/2}$ = 100 MHz for amorphous Se, and 115 MHz for Te. If $\langle\nu_Q^2\rangle^{1/2}$ is the same in the liquid, the correlation times for liquid Te and liquid Se at low temperature are given by

$$t_c^{-1} = \nu_0 \exp(-E/kT), \qquad (6)$$

where ν_0 = 8×10^{11} sec^{-1} for Se, 2×10^{15} sec^{-1} for Te, and E = 0.36 eV for Se, 0.56 eV for Te. For Se, we have previously conjectured[2] that the low temperature t_c is the Cd tracer diffusion time. The prefactor for Se is consistent with this suggestion, since ν_0 is the correct order of magnitude for a lattice vibration frequency. For liquid Te, t_c clearly cannot be the tracer diffusion time, since ν_0 is much larger than typical lattice vibration frequencies. It is presently not clear whether t_c in Te or in high-temperature Se is associated with chalcogen bond-breaking. We hope that additional measurements on amorphous solids and Te-rich liquid alloys may help to resolve these questions.

REFERENCES

*Research supported in part by the U.S. Office of Naval Research.

**Permanent Address: Department of Physics, University of Maryland Baltimore County, Baltimore MD 21228

1) R. L. Rasera and J. Gardner, Phys. Rev. B18 (1978) 6856.

2) D. K. Gaskill, J. A. Gardner, K. S. Krane, K. Krusch, and R. L. Rasera, in: Nuclear and Electron Resonance Spectroscopies Applied to Materials Science, eds. E. N. Kaufmann and G. K. Shenoy (North-Holland, Amsterdam, 1981) pp. 369-373.

3) H. Frauenfelder and R. M. Steffen, in: Alpha- Beta- and Gamma-Ray Spectroscopy, ed. Siegbahn (North-Holland, Amsterdam, 1965) Chap. 14, A.

4) A. Abragam and R. V. Pound, Phys. Rev. 92 (1953) 943.

5) K. Krusch and J. A. Gardner, Phys. Rev. B24 (1981) 4587.

6) D. K. Gaskill, to be published.

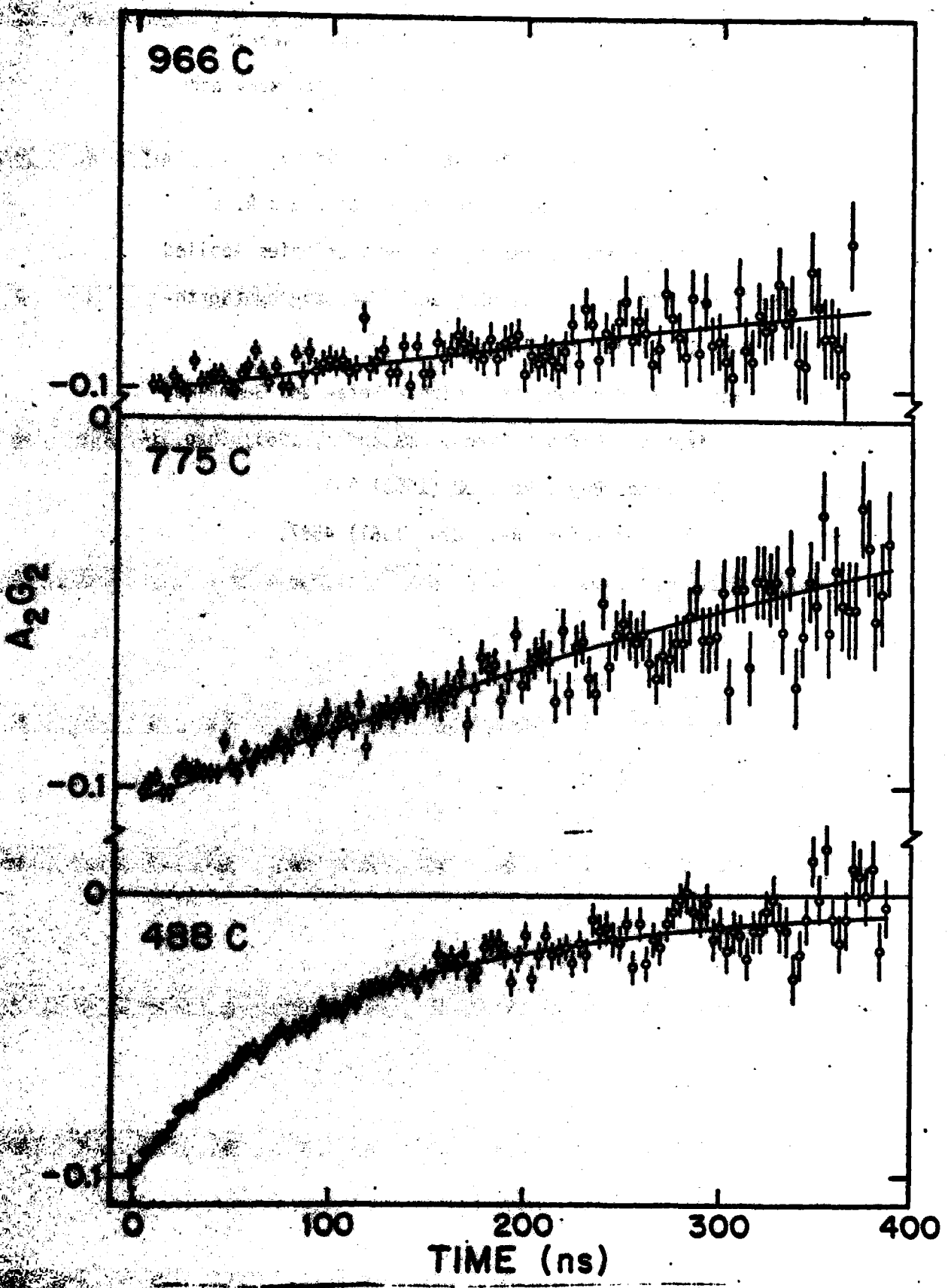


Figure 1. R(t) vs. time for ^{111}Cd in liquid Se at three temperatures. The solid lines are best fits to Equation 4.

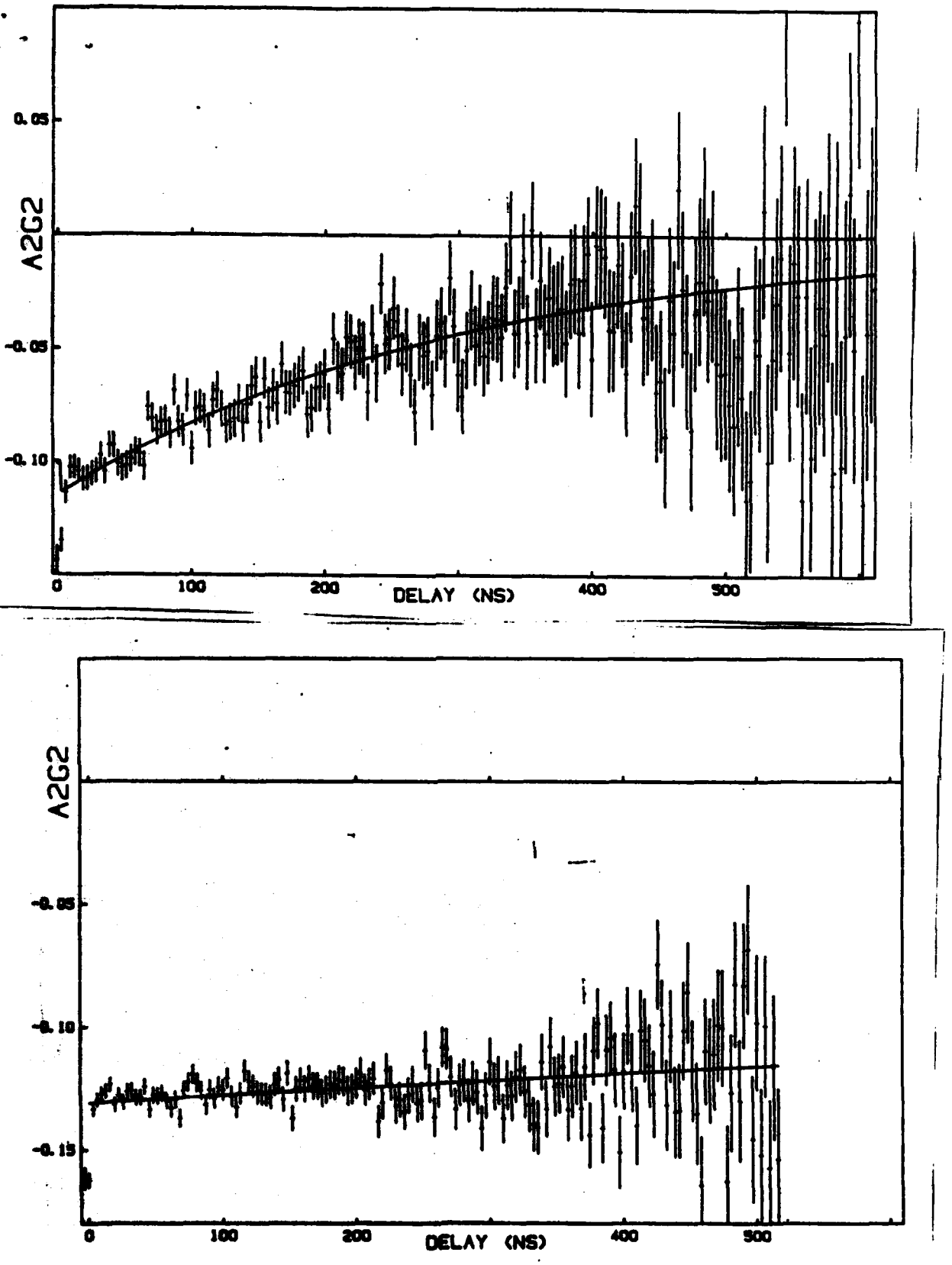


Figure 2. R(t) vs. time for ^{111}Cd in supercooled liquid Te at 269°C (top) and 416°C (bottom). The solid lines are best fits to Equation 4.

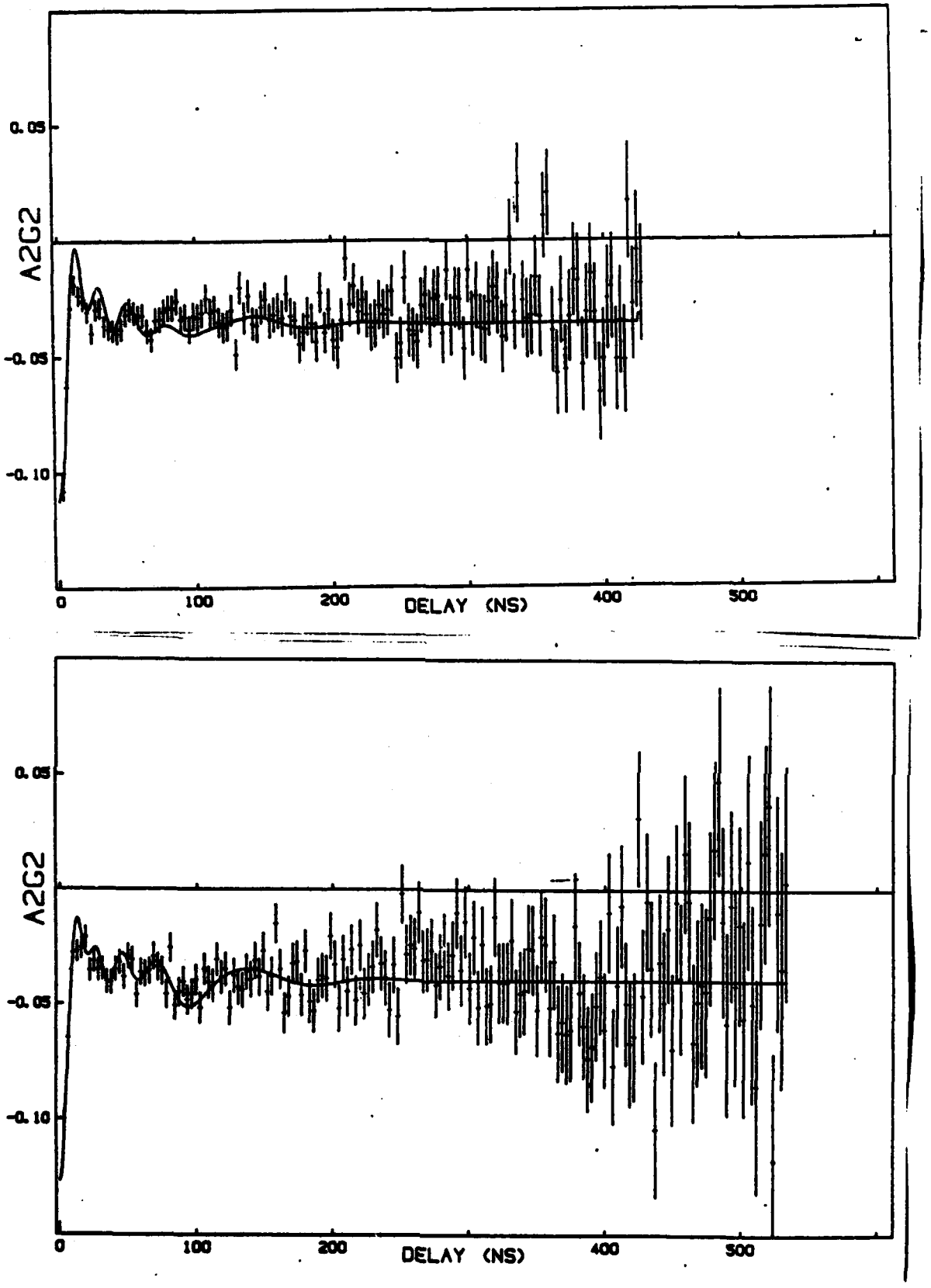


Figure 3. R(t) vs. time for ^{111}Cd in amorphous splat-quenched Se (top) and Te (bottom) at 78 K. The solid lines are best fits to Equation 3.

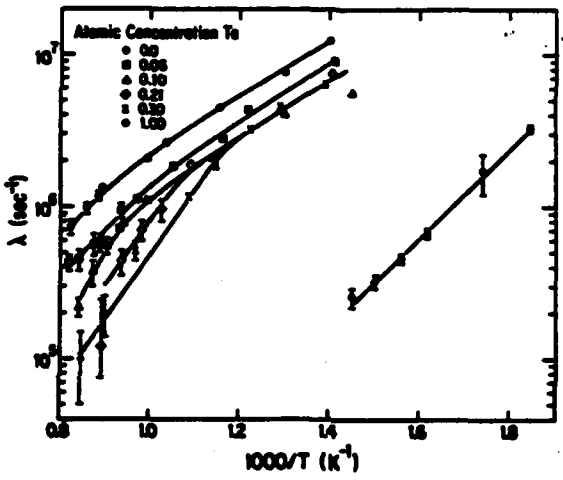


Figure 4. λ_{22} vs. inverse temperature for ^{111}Cd in liquid $Se_{1-x}Te_x$ alloys.

472:GAN:716-4
94/GEN

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Office of Naval Research Attn: Code 413 800 North Quincy Street Arlington, Virginia 22217	2
ONR Pasadena Detachment Attn: Dr. R. J. Marcus 1030 East Green Street Pasadena, California 91106	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12
Dr. Fred Saalfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1
U.S. Army Research Office Attn: CRD-AA-IP P. O. Box 12211 Research Triangle Park, N.C. 27709	1
Mr. Vincent Schaper DTNSRDC Code 2803 Annapolis, Maryland 21402	1
Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1
Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
Dean William Tolles Naval Postgraduate School Monterey, California 93940	1
Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Mr. A. M. Anzalone Administrative Librarian PLASTEC/ARRADCOM Bldg 3401 Dover, New Jersey 07801	1

TECHNICAL REPORT DISTRIBUTION LIST, 056

	No. Copies
Dr. G. A. Somorjai Department of Chemistry University of California Berkeley, California 94720	1
Dr. J. Murday Naval Research Laboratory Surface Chemistry Division (6170) 455 Overlook Avenue, S.W. Washington, D.C. 20375	1
Dr. J. B. Hudson Materials Division Rensselaer Polytechnic Institute Troy, New York 12181	1
Dr. Theodore E. Madey Surface Chemistry Section Department of Commerce National Bureau of Standards Washington, D.C. 20234	1
Dr. J. M. White Department of Chemistry University of Texas Austin, Texas 78712	1
Dr. Keith H. Johnson Department of Metallurgy and Materials Science Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1
Dr. J. E. Demuth IBM Corporation Thomas J. Watson Research Center P. O. Box 218 Yorktown Heights, New York 10598	1
Dr. C. P. Flynn Department of Physics University of Illinois Urbana, Illinois 61801	1
Dr. W. Kohn Department of Physics University of California (San Diego) La Jolla, California 92037	1
Dr. R. L. Park Director, Center of Materials Research University of Maryland College Park, Maryland 20742	1
Dr. W. T. Peria Electrical Engineering Department University of Minnesota Minneapolis, Minnesota 55455	1
Dr. Chia-wei Woo Department of Physics Northwestern University Evanston, Illinois 60201	1
Dr. Robert M. Hexter Department of Chemistry University of Minnesota Minneapolis, Minnesota 55455	1
Dr. R. P. Van Duyne Chemistry Department Northwestern University Evanston, Illinois 60201	1
Dr. S. Sibener Department of Chemistry James Franck Institute 5640 Ellis Avenue Chicago, Illinois 60637	1
Dr. M. G. Lagally Department of Metallurgical and Mining Engineering University of Wisconsin Madison, Wisconsin 53706	1

TECHNICAL REPORT DISTRIBUTION LIST, 056

	No. Copies
Dr. Robert Gomer Department of Chemistry James Franck Institute 5640 Ellis Avenue Chicago, Illinois 60637	1
Dr. R. G. Wallis Department of Physics University of California, Irvine Irvine, California 92664	1
Dr. D. Ramaker Chemistry Department George Washington University Washington, D.C. 20052	1
Dr. P. Hansma Physics Department University of California, Santa Barbara Santa Barbara, California 93106	1
Dr. J. C. Hemminger Chemistry Department University of California, Irvine Irvine, California 92717	1
Dr. Martin Fleischmann Department of Chemistry Southampton University Southampton 509 5NH Hampshire, England	1
Dr. G. Rubloff IBM Thomas J. Watson Research Center P. O. Box 218 Yorktown Heights, New York 10598	1
Dr. J. A. Gardner Department of Physics Oregon State University Corvallis, Oregon 97331	1
Dr. G. D. Stein Mechanical Engineering Department Northwestern University Evanston, Illinois 60201	1
Dr. K. G. Spears Chemistry Department Northwestern University Evanston, Illinois 60201	1
Dr. R. W. Plummer University of Pennsylvania Department of Physics Philadelphia, Pennsylvania 19104	1
Dr. E. Yeager Department of Chemistry Case Western Reserve University Cleveland, Ohio 41106	1
Professor D. Hercules University of Pittsburgh Chemistry Department Pittsburgh, Pennsylvania 15260	1
Professor N. Winograd The Pennsylvania State University Department of Chemistry University Park, Pennsylvania 16802	1
Professor T. F. George The University of Rochester Chemistry Department Rochester, New York 14627	
Professor Dudley R. Herschbach Harvard College Office for Research Contracts 1350 Massachusetts Avenue Cambridge, Massachusetts 02138	1
Professor Horia Metiu University of California, Santa Barbara Chemistry Department Santa Barbara, California 93106	
Professor A. Steckl Rensselaer Polytechnic Institute Department of Electrical and Systems Engineering Integrated Circuits Laboratories Troy, New York 12181	

472:GAN:716-4
94/056

TECHNICAL REPORT DISTRIBUTION LIST, 056

	No. Copies		No. Copies

Dr. John T. Yates
Department of Chemistry
University of Pittsburgh
Pittsburgh, Pennsylvania 15260

Professor G. H. Morrison
Department of Chemistry
Cornell University
Ithaca, New York 14853

Captain Lee Myers
AFOSR/NC
Bolling AFB
Washington, D.C. 20332

Dr. David Squire
Army Research Office
P. O. Box 12211
Research Triangle Park, NC 27709

Professor Ronald Hoffman
Department of Chemistry
Cornell University
Ithaca, New York 14853